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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/152186> since

Publisher:

Bro University

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Photocatalytic processes on TiO₂-Reduced Graphene Oxide hybrid materials: UV-based, dye-sensitized or visible-sensitized photocatalysis?

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Abstract

Graphene oxide (GO) was adsorbed on TiO₂ and chemically reduced at RT. Hybrid materials with different reduced GO (rGO) loadings were produced on anatase and silica and their photocatalytic activity was compared with pristine materials using phenol and methylene blue (MB) under two different irradiation conditions (UV-Vis and Vis only). The aim was to clarify the role of rGO in the photocatalytic mechanism. MB is strongly adsorbed at the surface of the hybrid materials, and the amount of adsorbed dye increases with increasing the rGO loading. Significant MB degradation rates were observed with pristine titania and with hybrid TiO₂-rGO materials, both under UV-Vis and Vis only. The presence of rGO had the largest effects on the degradation kinetics under Vis light. The absence of MB degradations with rGO-silica excludes that MB could inject electrons to rGO. MB is rather degraded by injecting photoexcited LUMO electrons in the TiO₂ conduction band. Therefore, the degradation under Vis-light is due to a dye-sensitized photocatalytic mechanism, while under UV-Vis the semiconductor-based photocatalytic mechanism is working. The role of rGO seems to be limited to that of adsorbent. Conversely, the presence of rGO reduces the rate of photocatalytic transformation for the poorly adsorbed phenol under UV-irradiation, while negligible transformation rates were observed under Vis on both pure titania and TiO₂-rGO. No photocatalytic mechanism is thus operating in the visible. The analysis of UV-Vis absorption spectra at different rGO loadings shows that the decrease of phenol degradation under UV is due to the decrease of the band-gap absorption of TiO₂. From this set of experimental data, it emerges that the beneficial effect of rGO at the TiO₂ surface is related only to the increase of adsorption. Therefore, inferences drawn by single-substrate experiments, particularly with dyes (e.g. MB), or with a single irradiation type can be misleading.